Periodic Slab LAPW Computations for Ferroelectric BaTiO$_3$

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Abstract

Linearized augmented plane wave (LAPW) calculations are performed for periodic (001) and (111) slabs of BaTiO$_3$ to understand the effects of surfaces on ferroelectric BaTiO$_3$. The (111) slab is found to be much less stable than the (001) slab. The average surface energies are respectively 3700 erg/cm^2 and 1600 erg/cm^2. The depolarization field is sufficiently large in the ideal unrelaxated slab to completely inhibit the ferroelectric instability. No mid-gap surface states are evident, but there are surface states in the upper gap in the unrelaxed slab and at the top of the valence band. The dangling surface Ti bonds self-heal making the Ti-O surface very reactive and an excellent epitaxial substrate. The charge density on atoms only one unit cell away from the surface are almost identical to the bulk.

Keywords: ferroelectric, surface, slab, electronic structure, depolarization, BaTiO$_3$, thin film

I. INTRODUCTION

Although ferroelectricity is a bulk property, surfaces are crucial for real ferroelectrics. The termination of an ideal, ionic ferroelectric gives rise to a huge depolarization field, E_d, of opposite sign to the bulk polarization, giving a contribution to the energy of $-E_d \cdot P$

large enough to completely destabilize the bulk ferroelectric state [1] p. 94; [2]. Properties of ferroelectric films vary with film thickness [3] and become cubic when thin. Huge particle size effects are observed [4,5] which again illustrate the importance of surfaces.

Experimental studies of $BaTiO_3$ surfaces are few and many more studies have focused on $SrTiO_3$ which lacks the complications of ferroelectricity. Photoemission studies of sputtered and annealed $BaTiO_3$ show evidence of significant surface defects [6], so intrinsic surface states could not be easily delineated. Studies of $SrTiO_3$ surfaces show evidence for minor relaxations by motions of atoms perpendicular to the surfaces [7] and show no evidence for states in the gap [8]. A tight-binding model for $SrTiO_3$ predicted Ti 3d-surface states in the gap [9], inconsistent with the observations [8], and only after including a coulomb repulsion parameter U_d in their model did the states move out of the gap [10]. No self-consistent calculations for surfaces of $BaTiO_3$ or $SrTiO_3$ have been done. Molecular X_α calculations give some insights into possible surface effects and give insight into effects of Madelung fields and charge relaxation at surfaces [11]. Very recent photoemission spectroscopy on $BaTiO_3$ shows excellent agreement with bulk LAPW computations of the LDA band structure [12]. See [13] for a review of the properties of oxide surfaces. First-principles electronic structure approaches have been very successful for bulk ferroelectrics [14-21] but the application of first-principles band structure methods to surface properties is daunting due to the giant computational burden. Here the first set of accurate electronic structure calculations for periodic $BaTiO_3$ slabs are presented. It is not possible to fully explore surface relaxations and interactions between relaxations and bulk ferroelectricity, which is an ultimate goal of this work. Nevertheless, these results can be considered benchmark results for faster, more approximate methods, and also give some insights into the electronic structure of ferroelectric $BaTiO_3$ surfaces.

II. METHOD

Three layer, 15 atom, (001) and (111) periodic slabs of BaTiO$_3$ were studied using the Linearized Augmented Plane Wave with extra local orbitals (LAPW+LO) method [22] in the ideal configuration, and the more stable (001) slab was studied in the ideal configuration, with a tetragonal ferroelectric distortion, and with some surface relaxations. A vacuum region of the same thickness as the slab separates the periodic slabs. The ideal slabs are illustrated in figure 1. The (001) slab has 4mm tetragonal symmetry with eight-space group operations, and the (111) slab is rhombohedral with 3m symmetry. The (001) slab has two types of surfaces, both charge-balanced . One surface contains Ti and O in a ratio of 1:2 and the other consists of equal amounts of Ba and O. The (111) slab has quite unstable looking surfaces as shown in figure 1.

The lattice constant (i.e. ideal Ba-Ba distance) was fixed at 7.57 bohr (4.006 Å), which gives an *a*-axis length of 7.57 bohr and *c*-axis length of 45.42 bohr (24.035 Å) for the (001) slab and 10.70 bohr for *a* and 26.2 bohr for *c* for the (111) slab. In order to obtain accurate energy differences and surface energies, bulk calculations were also performed in the same symmetry with a tripled supercell with the same k-points and convergence parameters.

The ferroelectric distortion in the (001) slab used the experimental tetragonal average displacements. The Ba's were displaced by 0.06 Å, the Ti's by -0.1122 Å along *c* relative to the O(II)'s, and the O(I)'s by 0.0288 Å . Displacements were performed in both directions, with Ti displaced towards the Ba-O surface and towards the Ti-O surface. The tetragonal phase in bulk BaTiO$_3$ does not consist primarily of displacements towards the perovskite cube faces, as we are studying here, but rather displacements towards the cube diagonals, and the tetragonal structure is a dynamical average with hopping among four [111] directions. Such disordered configurations are well beyond the possibilities of present computations for slabs, and must await future faster and probably more approximate methods. Nevertheless, the general effects of a surface on ferroelectric properties can be illuminated by the present study.

Two simple surface relaxations in ferroelectric $BaTiO_3$ derived from experiment [7] on $SrTiO_3$ were also studied. The first was a dimpling of the Ba-O plane by moving the Ba in by 0.22 Å. Actually, the ferroelectric distortion moves this Ba out of the slab away from the O plane by 0.06 Å, so this "relaxation" moves the Ba in by 0.16 Å from the O surface plane. The second "relaxation" was to displace the surface Ti out by 0.056 Å as suggested by the RHEED results for $SrTiO_3$. Actually, the relaxations used are not precisely those determined experimentally since only the dimpling was included here, and not the change in average layer spacing. Thus even the limited relaxation effects shown here should be considered very preliminary estimates.

The muffin tin radii were 2.3 bohr for Ba, 1.75 bohr for Ti, and 1.75 for O, and the convergence parameter RK_{max} was set to 7.0. A 4×4×2 special k-point mesh was used which gives 3 k-points for the (001) slab and 10 k-points for the (111) slab. For the (111) slab a 2×2×2 mesh was also used and the surface energy differs from the larger k-point set by only 0.4%. The matrix order (number of basis functions) for the slabs was about 2900. These calculations are extremely computationally intensive. Not only was each iteration in the self-consistent cycle time consuming (about 11 hours on one processor on the Convex C3 at NCSA) but an unusually large number of iterations were required to reach self-consistency due to charge fluctuations across the slab set up by the electric fields generated across the slab.

III. RESULTS AND DISCUSSION

Table 1 shows the total energy results. The first order results are the surface energies. Since we are not studying isolated slabs, but rather periodic slabs, there are long-range electrostatic interactions between the periodic images. The results given here have not been corrected for these interactions, so that the surface energies would be somewhat higher than given here from this approximation. On the other hand, we have not fully relaxed any of the slabs, which would lower the surface energy. The numbers given here can thus be considered

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only as initial estimates. The energies shown in Table 1 give the cleavage energy, and half of the cleavage energy is the average surface energy for the two types of surfaces formed on cleavage. For the (111) slab an average surface energy of 3700 erg/cm^2 is obtained, and for the more stable (001) surface the energy is 1600 erg/cm^2. These are quite reasonable values. For comparison, the unrelaxed surface energy for Cr_2O_3 is estimated to be 2800 erg/cm^2 and 2000 erg/cm^2 for the relaxed surface [23]. The surface energy of SiO_2 glass is much lower, about 300 erg/cm^2. We have not fully relaxed the surface, but although the relaxation of the Ba atom in towards the slab reduces the surface energy by several percent, it is a negligible change considering the approximations such as neglecting the slab interaction energies.

The depolarization field at the surface does indeed destroy the ferroelectric instability, and the energy goes up by 6-60 times the bulk well depth using the average bulk ferroelectric displacements, so the ferroelectric destabilization energy from the depolarization field for the perfect slab is many times greater than the bulk ferroelectric instability.

The two surface "relaxations" are also quite interesting. The energy gain on displacing the Ba ions towards the interior of the slab is much greater than even the bulk ferroelectric well, so that ionic motions on surfaces could indeed dominate the bulk energetics. This may be the ultimate cause of the size effects observed for ferroelectrics. Displacing the surface Ti ions actually increased the energy. This may be due to the ferroelectric distortion in $BaTiO_3$.

There has been much discussion about possible electronic surface states in $BaTiO_3$. Calculated band structures for the bulk and ideal slab are shown in figure 2. No midgap surface states are found, consistent with experiment. However, the gap is smaller due to the surfaces so unoccupied states at the top of the gap are predicted. It is possible that these would move up into the bulk conduction band in a fully relaxed slab. Also, there is an interesting surface state at M; the topmost occupied state is a pure O p state on the Ti-O surface, not a Ti d-state as has been discussed from cluster or approximate calculations [9-11].

The most intriguing results are an examination of the self-consistent charge densities.

Figure 3a shows the differences in total charge density between the self-consistent LAPW results for the (001) slab and overlapping spherical ions. The bonds between the O and Ti are clearly evident. Most interesting is the collapse of the surface Ti bond. Instead of dangling the charge moves back onto the Ti and the Ti-O surface bonds. This self-healing leaves the surface highly reactive, and is probably responsible for the utility of $BaTiO_3$ as a substrate for epitaxial growth and for surface catalysis. The Ba-O surface shows much less difference from spherical ions, and is found to be highly ionic. These results suggest that the Ti-O surface of $BaTiO_3$ is highly reactive due to the possibility of covalent bonding on the surface, whereas any reactivity Ba-O surface is due entirely to ionic bonding. The non-bonding O p surface state may also enhance surface reactivity.

Figure 3b shows the difference between the LAPW (001) slab density and the self-consistent LAPW charge density for bulk periodic $BaTiO_3$. Large changes are seen on the surface Ti, and smaller changes on the surface Ba and O. Most interestingly, the differences the interior Ti and O, which are only 1 unit cell away from the surface, are almost identical to bulk Ti and O. This shows that electronic perturbations due the surface are screened very rapidly in the interior of a crystal. The screening is accomplished primarily due to polarization and charge redistributions around the surface Ti, and to a lesser extent, O ions.

IV. CONCLUSIONS

The first precise surface calculations for a ferroelectric are given here for $BaTiO_3$. These computations are extremely intensive, but will serve as benchmarks for more approximate but faster methods. It is found that energetics from surface relaxations sweep the energetics of the ferroelectric instability in $BaTiO_3$. The (001) surfaces are found to be much more stable than (111) surfaces, in agreement with experiment. Also in agreement with experiment no mid-gap surface states are found, but surface states do appear in the upper gap in the ideal slab and at the top of the valence band. The surface Ti-bond relaxes back

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into the surface and self-heals, making the Ti-O surface as excellent substrate for epitaxial growth. Even one layer in from the surface the charge density is almost identical to the bulk indicating that electronic surface effects do not extend deeply into the solid.

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Table 1. Energetics of BaTiO$_3$ slabs and bulk BaTiO$_3$.

	$E + 55258 Ryd$	$\Delta E(eV/5atoms)$	$\Delta E(eV/5atoms)$
symmetric bulk	-0.3586	0.0	
bulk ferroelectric		-0.005	
ideal (001) slab	-0.1189	1.087	0.0
ferroelectric slab (+)	-0.1119	1.119	0.032
ferroelectric slab (−)	-0.0482	1.408	0.321
ferroelectric slab (Ba in)	-0.1235	1.066	-0.021
ferroelectric slab (Ti in)	-0.1058	1.146	0.059
bulk (111)	-0.3578	0.0	
ideal (111) slab	$+0.5740$	4.226	

VI. FIGURE CAPTIONS

1.BaTiO$_3$ slabs studied. Red is Ti, green is Ba, and blue is Ti. a) (111) slab. b) (001) slab.

2. Band structures for BaTiO$_3$. a) Bulk band structure for cubic BaTiO$_3$ folded into the Brillouin zone for the triple supercell. b) Band structure for the ideal undistorted three-layer slab.

3. Charge density for BaTiO$_3$ slab. a) Deformation charge density for BaTiO$_3$. The image shows the difference in charge density between the self-consistent LAPW charge density and overlapping PIB ions. Green represents no change in density (i.e. identical to the ionic crystal). Partially charged ions, Ba$^{1.63+}$, Ti$^{3.26+}$, O$^{1.63-}$ were used to generate the ionic charge density. Note the "healing" of the surface Ti dangling bond. It collapses back onto the Ti. b) Difference in charge density between the ideal slab and bulk BaTiO$_3$. Even though the slab is only three layers thick, the central layer has almost an identical charge density to bulk BaTiO$_3$, although there are still some small differences on the Ba.

a)

Ti 3d (conduction)

"O 2p" (valence)

Ba 5p

O2s

b)

a)

e/bohr^3

0.02

0.0

-0.02

b)

e/bohr^3

0.01

0.0

-0.01